Research in Energetic Ionic Liquids

October 2002

Greg Drake and Tommy Hawkins

gregory.drake@edwards.af.mil

tommy.hawkins@edwards.af.mil

High Energy Density Materials Research

AFRL/PRSP

Air Force Research Laboratory

⊛ Paper Rec'd After 30-day Deadline = 8- days until Deadline / Cont. Begins

FILE

MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO)

01 October 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-232**
Greg Drake (PRSP) et al., "Research in Energetic Ionic Liquids" (viewgraphs)

55355

AFOSR Workshop hosting gov't & academic researchers **(Statement A)**
(Dulles, VA, 9-10 October 2002)

Energetic Ionic Liquids

Before we get started….

People who have been and are critical to our research project

Tommy Hawkins
Kerri Tollison
Adam Brand and Milton Mckay
Lt. Leslie Hall and Ashwani Vij
Mike Berman AFOSR
Tommy Highsmith ATK/Thiokol
Mark Petrie /Jeff Bottaro SRI Int.
Mike Huggins
Jeff Sheehy

Energetic Ionic Liquids

Energetic Ionic Liquids- one of the new focal points for HEDM research. Why are we here today? HEDM research effort has shifted away from cryogenic/matrix isolation and now is pointing into synthetic endeavors

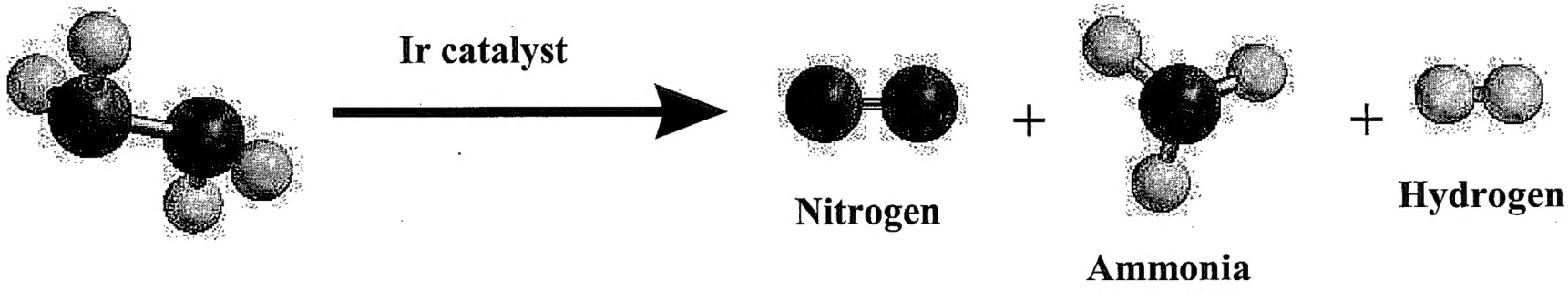
Goal: Build a solid working relationship between theoretical/computational and synthetic chemists as well as having work going on in decomposition areas in trying to fully understand energetic ionic liquids. Both sides of the fence need guidance from each other to be truly productive in a practical sense.

Ionic liquids have been around a very long time (100 years), and recently they have really taken off. But in this "take off" most researchers are looking for applications in the use of ionic liquids. Few people are looking at ionic liquids for the "why" these materials are low melting and how this unusual class of compounds might be more useful for other applications.

Our research at AFRL has been working on designing, synthesizing, and fully characterizing new low melting energetic salts which are useful.

Energetic Ionic Liquids

State of the art is hydrazine, N_2H_4, which is used in many satellite systems



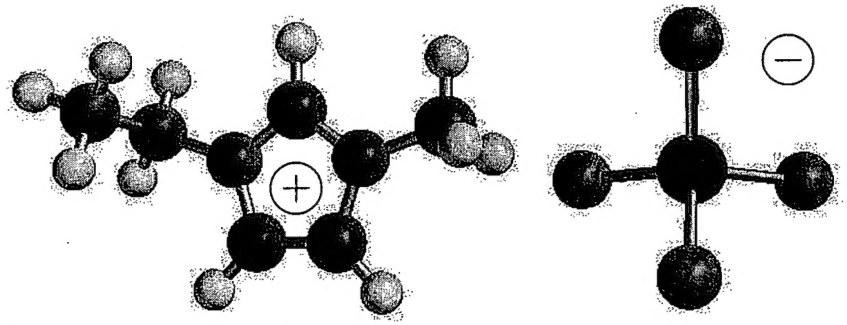
<u>Advantages:</u> Tried and true for several decades, relatively cool burning for hardware.

<u>Disadvantages:</u> Hydrazine is extremely toxic(carcinogenic), has a high vapor pressure, a high melting point (1^{o}C), and results in workers using self contained suits .

Our approach at AFRL has been investigating new low melting salts as they have inherent advantages including higher densities and negligible vapor pressures.

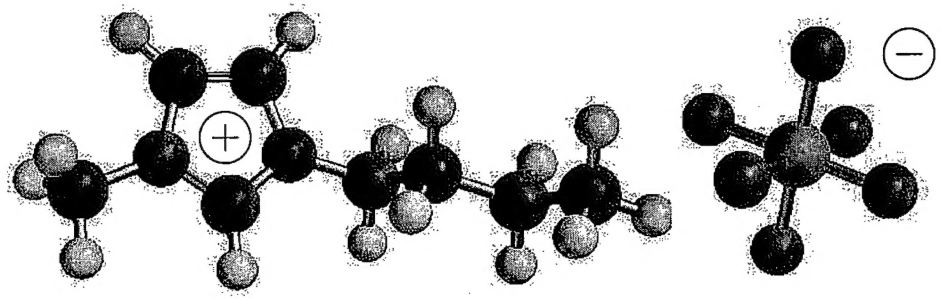
Energetic Ionic Liquids

Ionic liquids research was really opened up by the pioneering work of John Wilkes, Charles Hussey and others under USAF research looking for new battery electrolytes. Dealt heavily with aluminum halide anions early on.



1-ethyl-3-methylimidazolium tetrachloroaluminate

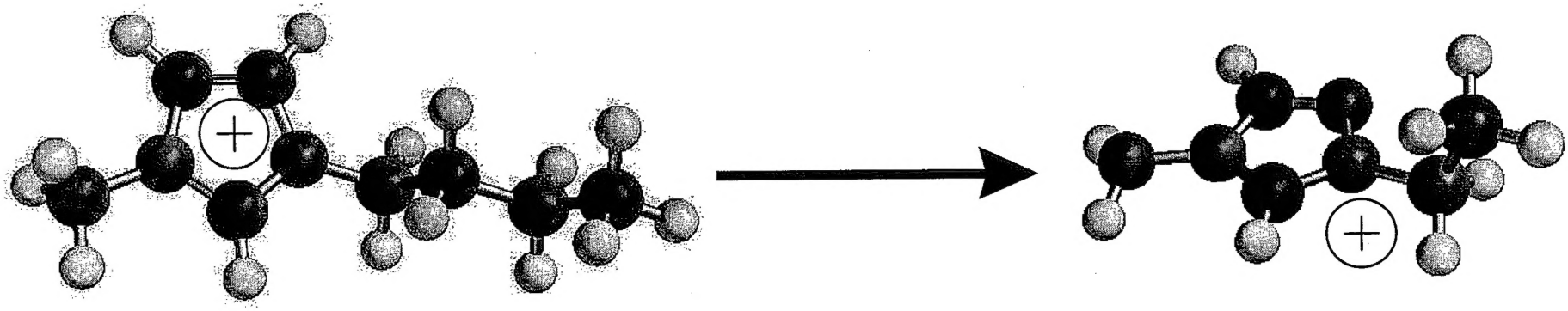
Later, water stable ionic liquids were synthesized by Wilkes and coworkers which opened up the currently rapidly expanding field that we see today.



1-butyl-3-methylimidazolium hexafluorophosphate

Energetic Ionic Liquids

Most ionic liquids are based upon imidazolium rings and "heavy" or "dead" anions. We felt that we could use the shape of the cation and the poor fit idea to make much more energetic salts in a simple manner.

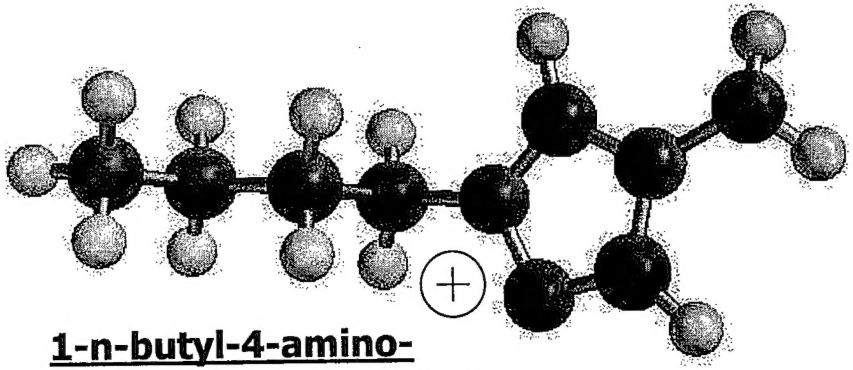


1-n-butyl-3-methyl imidazolium cation

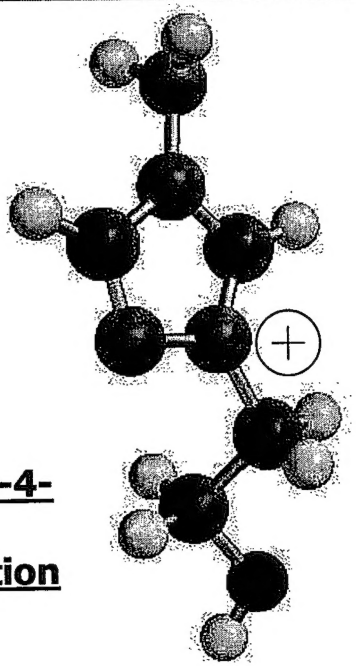
1-ethyl-4-amino-1,2,4-triazolium cation

AFRL energetic ionic liquids have similar shapes and physical properties, BUT higher ΔH_f, higher density, and better oxygen balances.

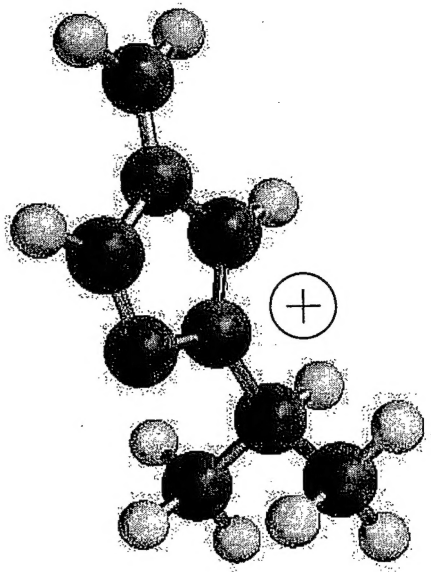
Energetic Ionic Liquids



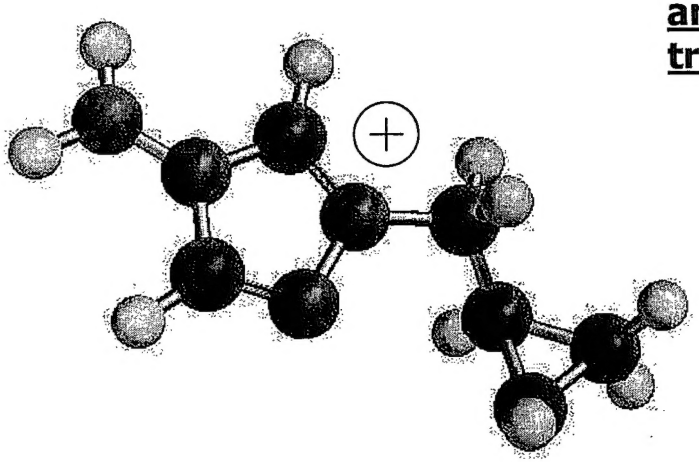
1-n-butyl-4-amino-
1,2,4-triazolium cation



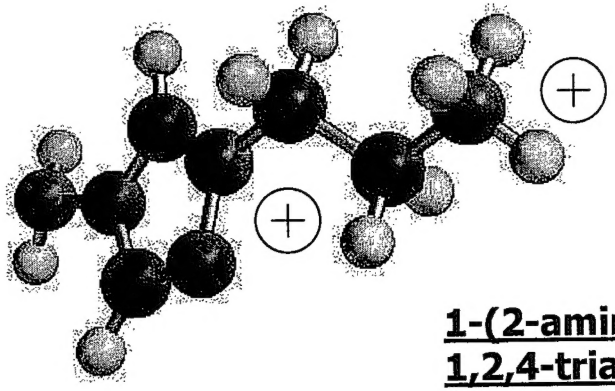
1-(2-ethanol)-4-
amino-1,2,4-
triazolium cation



1-isopropyl-4-amino-
1,2,4-triazolium cation

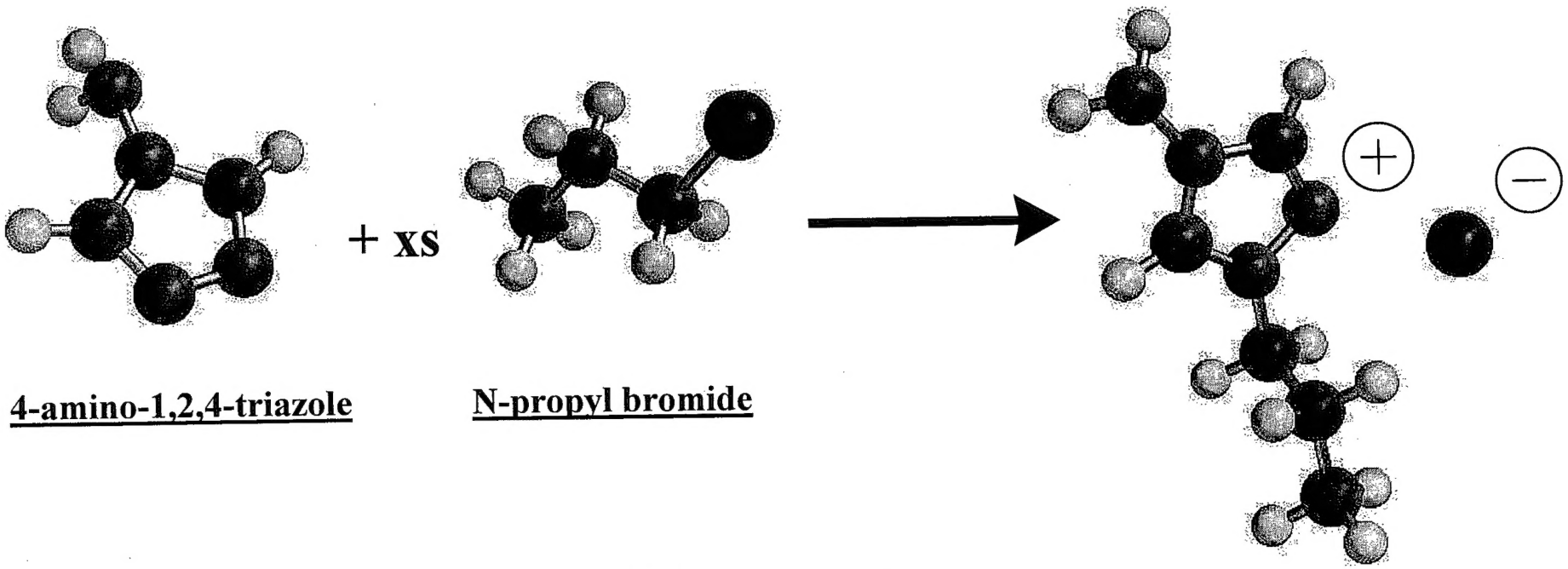


1-methylcyclopropyl-4-amino-
1,2,4-triazolium cation



1-(2-aminoethyl)-4-amino-
1,2,4-triazolium dication

Energetic Ionic Liquids



4-amino-1,2,4-triazole

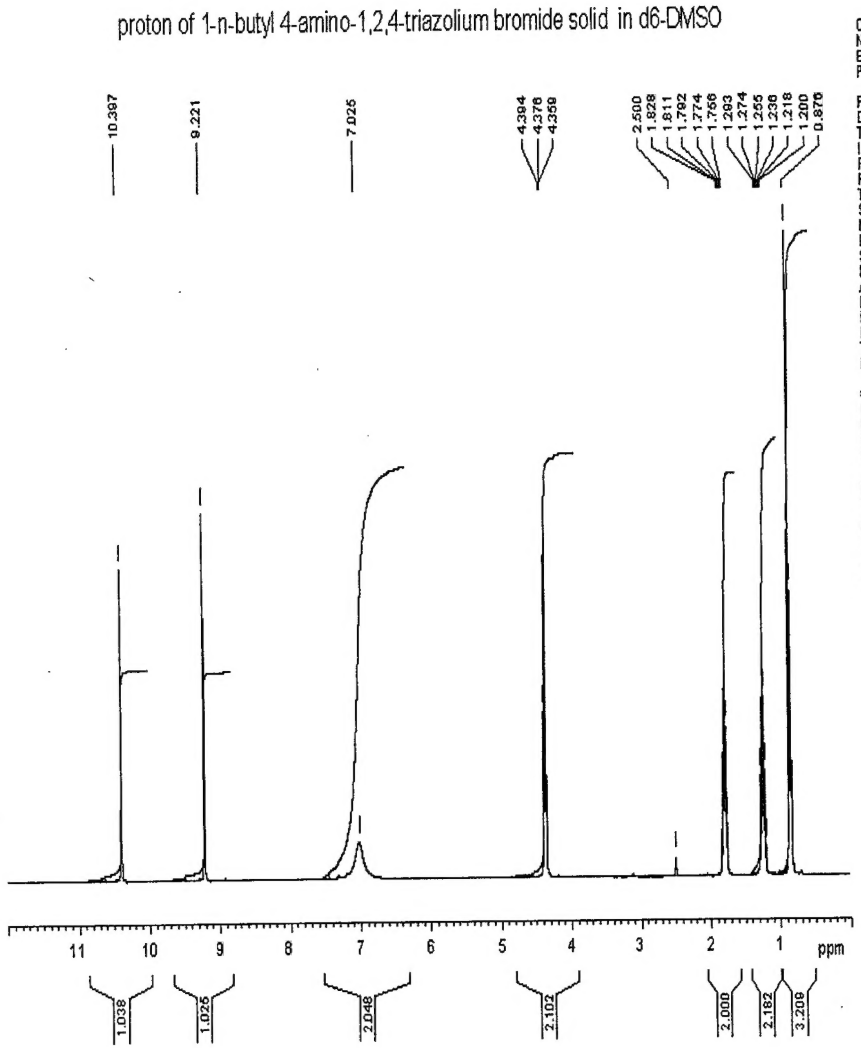
N-propyl bromide

Synthesis is from commercial materials
High yield simple isolation has been known in literature for quite sometime.

1-n-propyl-4-amino-1,2,4-triazolium bromide (yield >95% very pure)

Scriven; Keay; Goe; Astleford J. Org. Chem. **1989**, *54*, 731.

Energetic Ionic Liquids

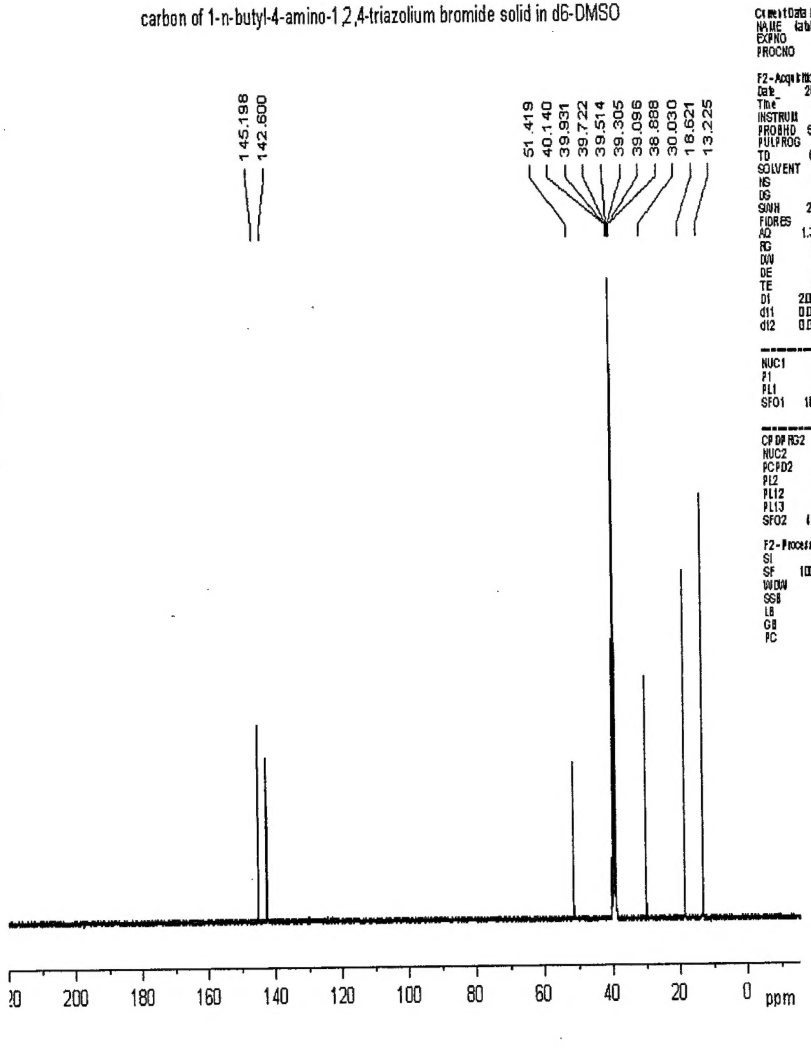


Current Data Parameters
NAME 4atnbutBrSarah
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020725
Time 10.46
INSTRUM spect
PROBHD 5 mm BBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 50.8
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

CHANNEL f1
NUC1 1H
P1 7.20 usec
PL1 -6.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300036 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME 4atnbut8rSarah
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020725
Time 11.15
INSTRUM spect
PROBHD 5 mm BBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1024
DS 4
SWH 25125.629 Hz
FIDRES 0.383381 Hz
AQ 1.3042164 sec
RG 32768
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

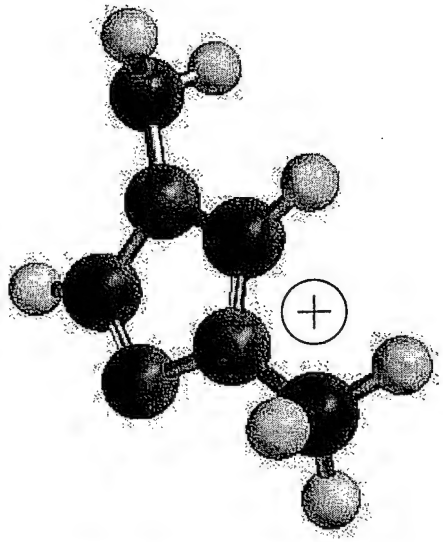
CHANNEL f1
NUC1 13C
P1 7.00 usec
PL1 -5.00 dB
SFO1 100.6237959 MHz

CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 18.00 dB
PL12 18.00 dB
PL13 120.00 dB
SFO2 400.1316005 MHz

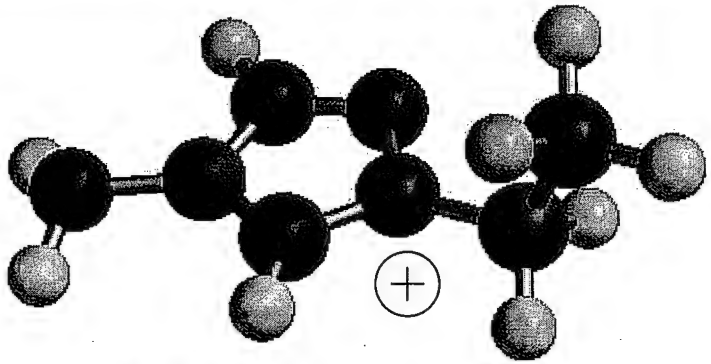
F2 - Processing parameters
SI 32768
SF 100.6128178 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{1}H(left) and ^{13}C nmr spectra of 1-butyl-4-amino-1,2,4-triazolium bromide.

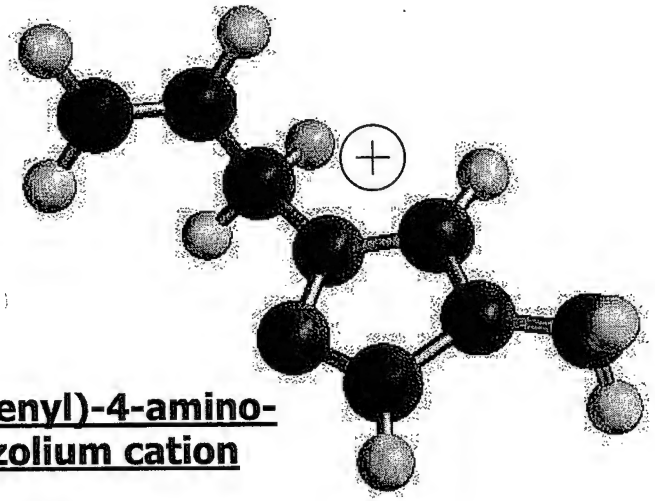
Energetic Ionic Liquids



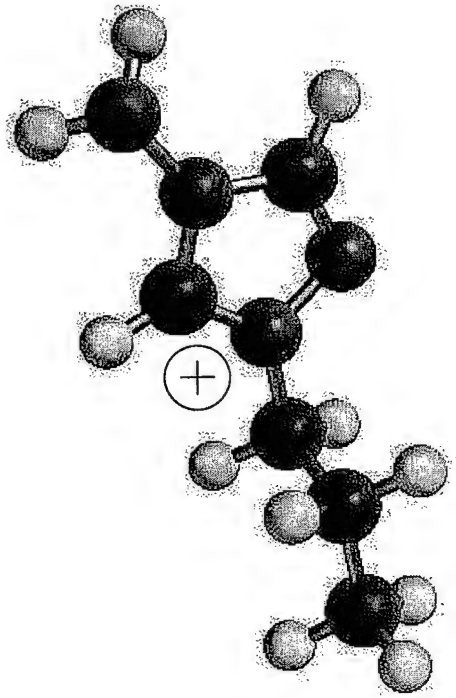
1-methyl-4-amino-
1,2,4-triazolium cation



1-ethyl-4-amino-
1,2,4-triazolium cation

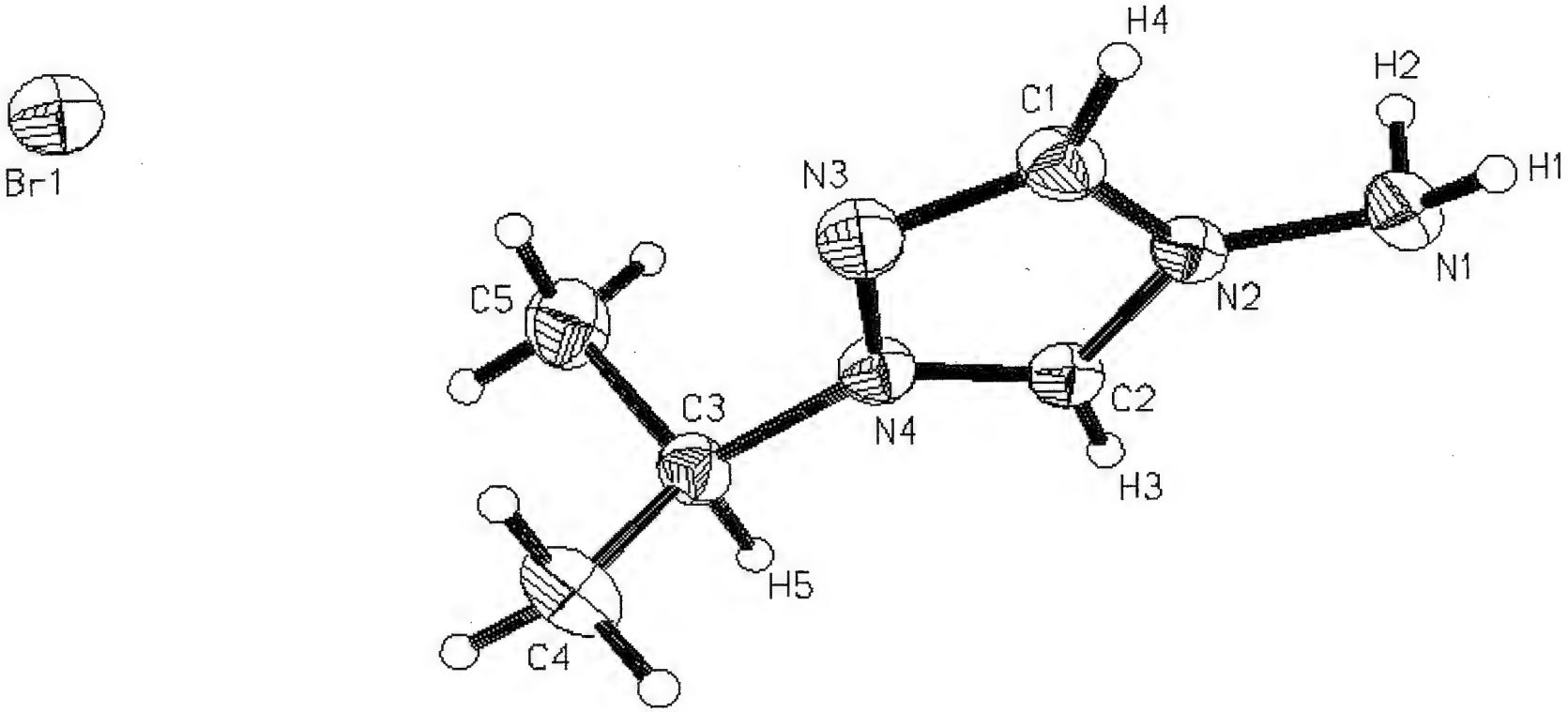


1-(2-propenyl)-4-amino-
1,2,4-triazolium cation



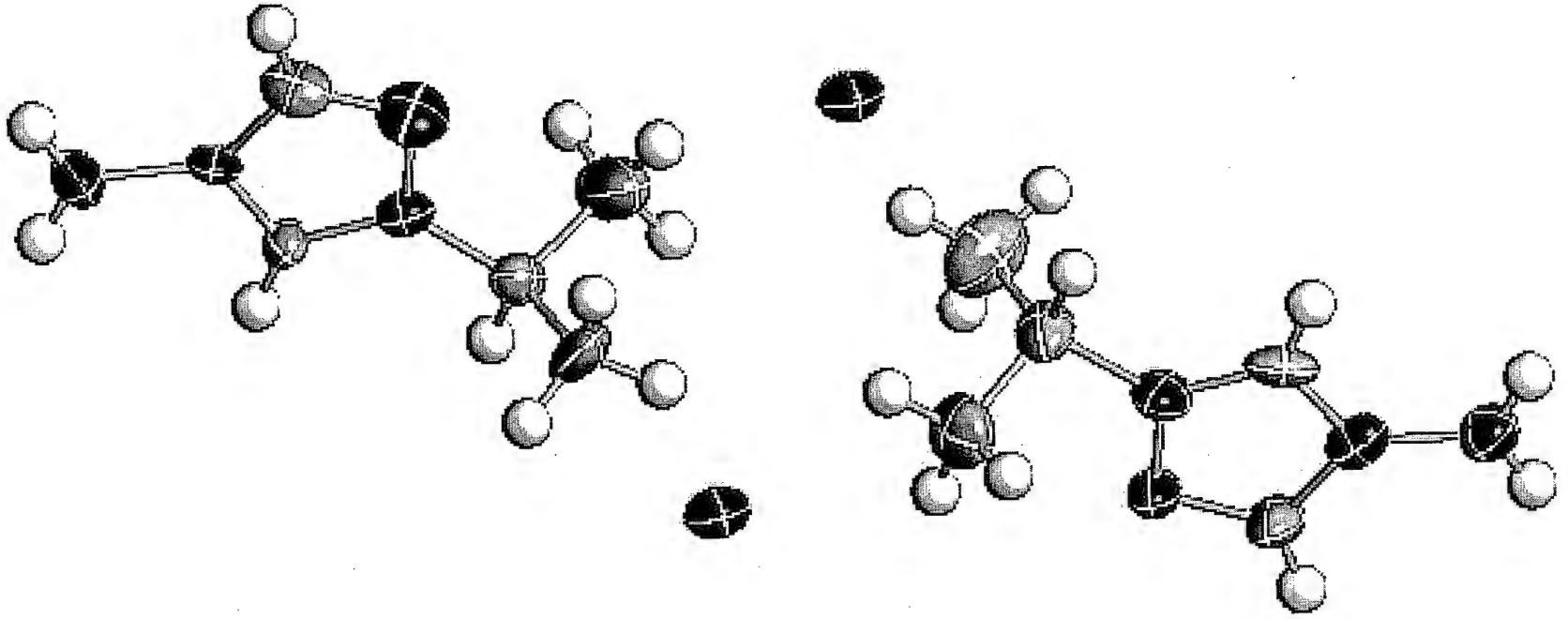
1-n-propyl-4-amino-
1,2,4-triazolium cation

Energetic Ionic Liquids



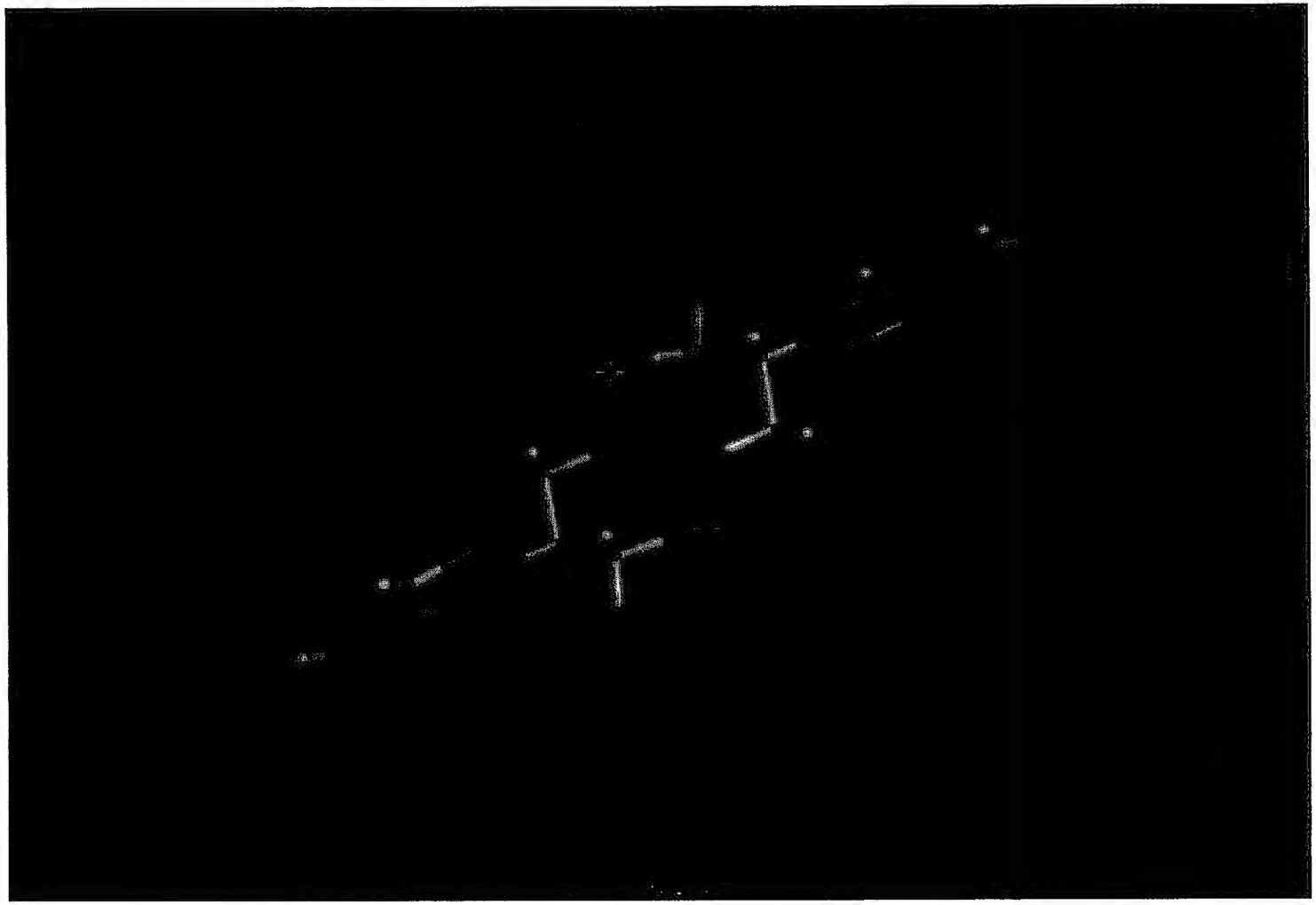
Single crystal x-ray diffraction study ORTEP view of 1-isopropyl-4-amino-1,2,4-triazolium bromide(Dr. A. Vij and Lt L. Hall)

Energetic Ionic Liquids



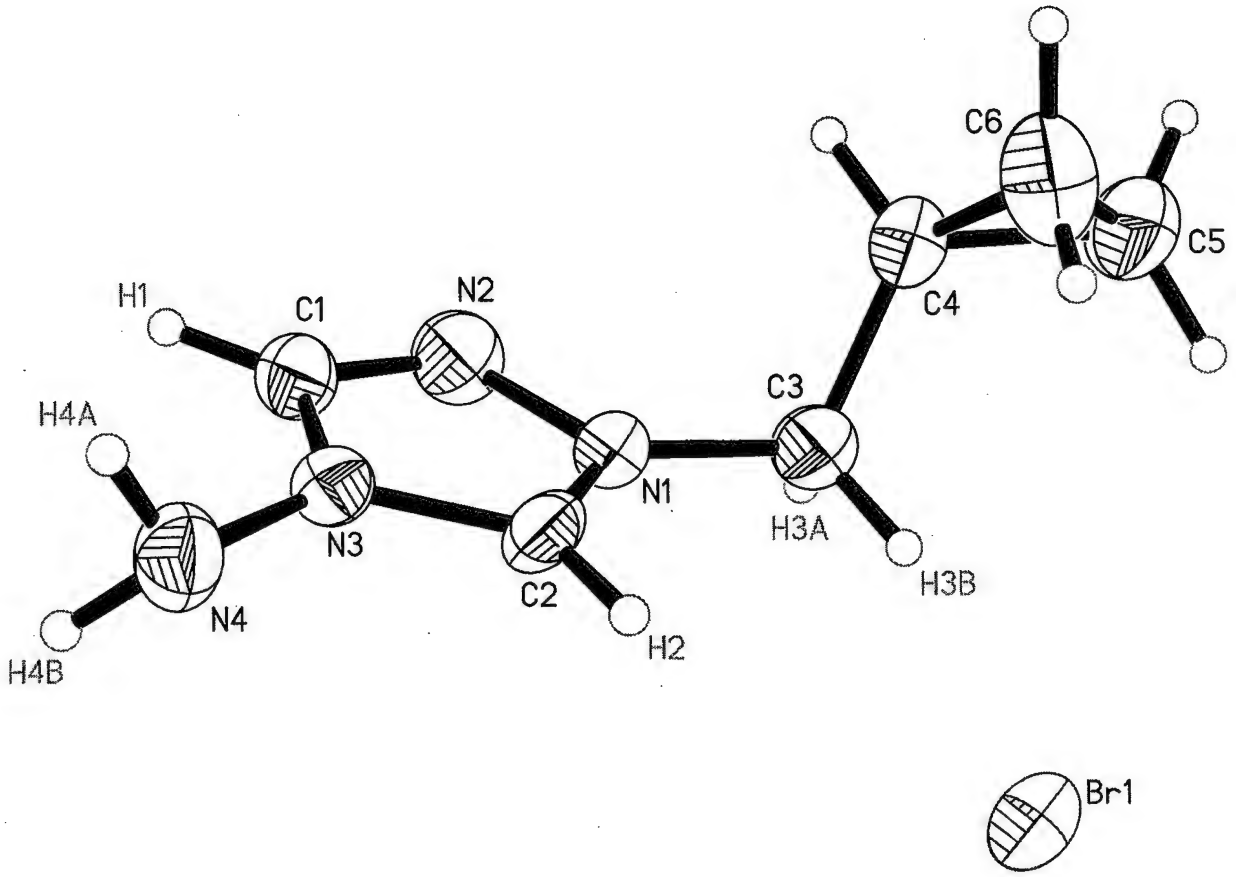
Single crystal x-ray diffraction study of 1-isopropyl-4-amino-1,2,4-triazolium bromide

Energetic Ionic Liquids



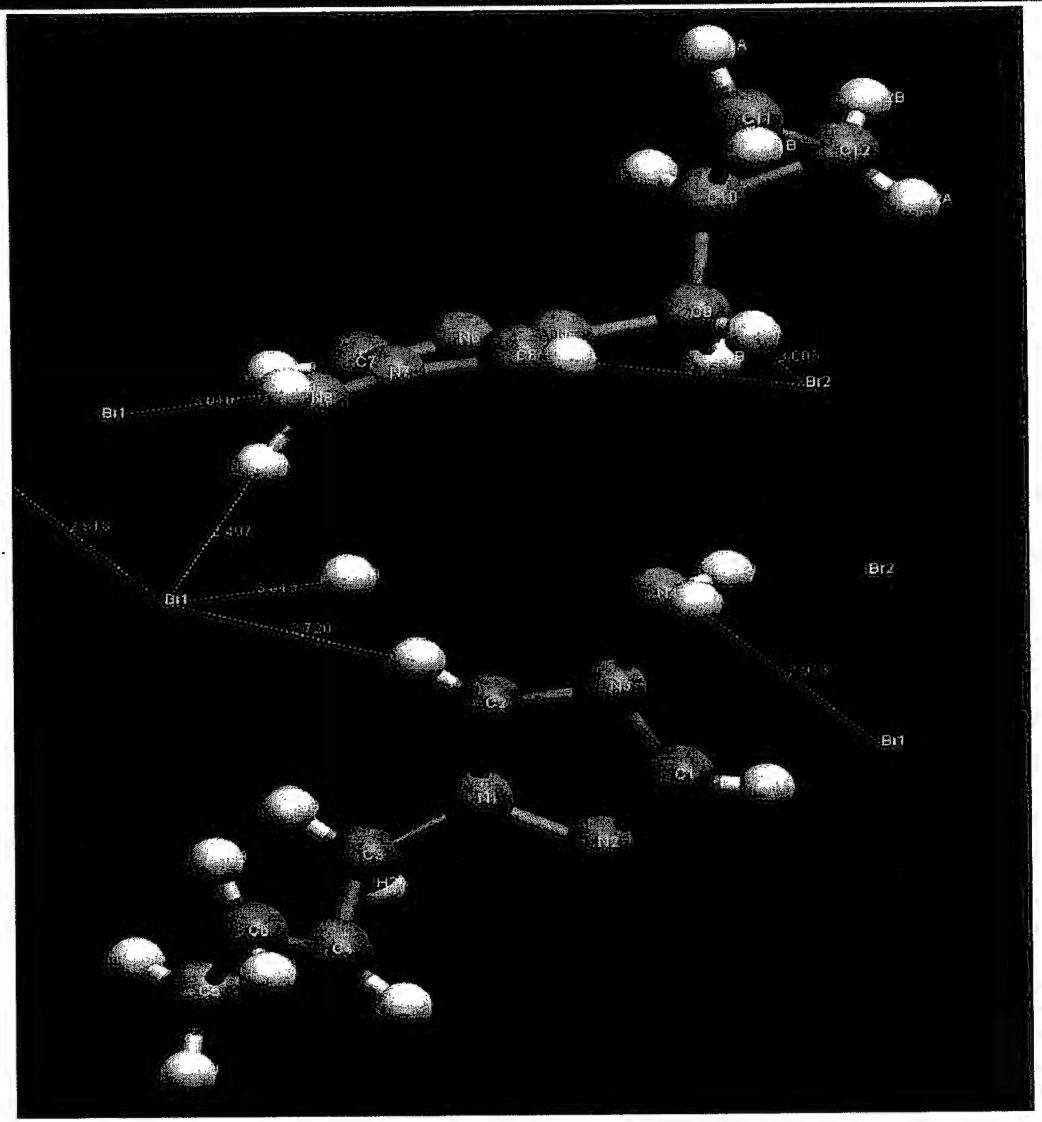
Single crystal x-ray diffraction study of 1-isopropyl-4-amino-1,2,4-triazolium bromide

Energetic Ionic Liquids



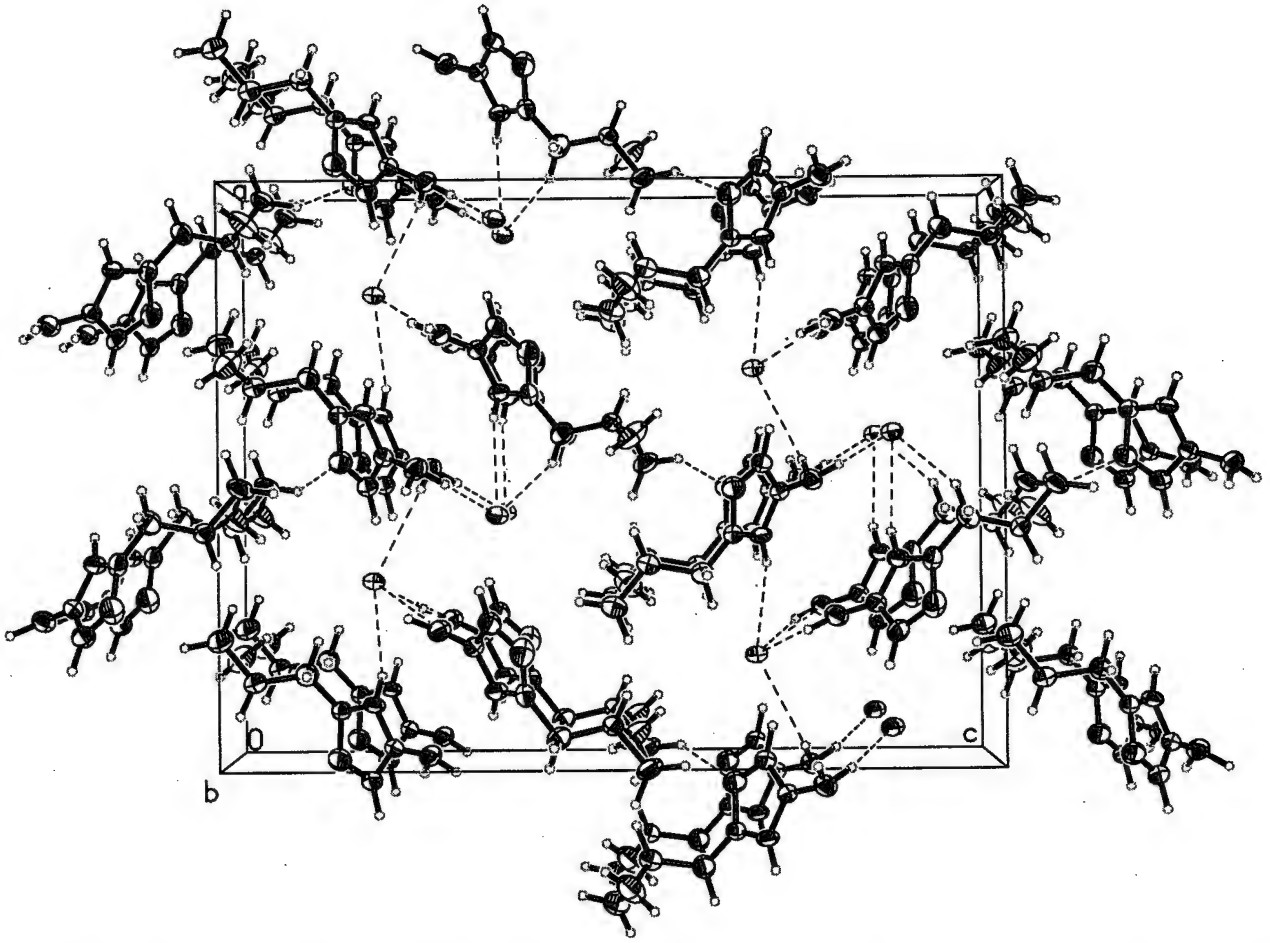
Single crystal x-ray diffraction study ORTEP view of 1-cyclopropylmethyl-4-amino-1,2,4-triazolium bromide(Dr. A. Vij and Lt L. Hall)

Energetic Ionic Liquids



Br--H-N interactions in 1-cyclopropylmethyl-4-amino-1,2,4-triazolium bromide

Energetic Ionic Liquids



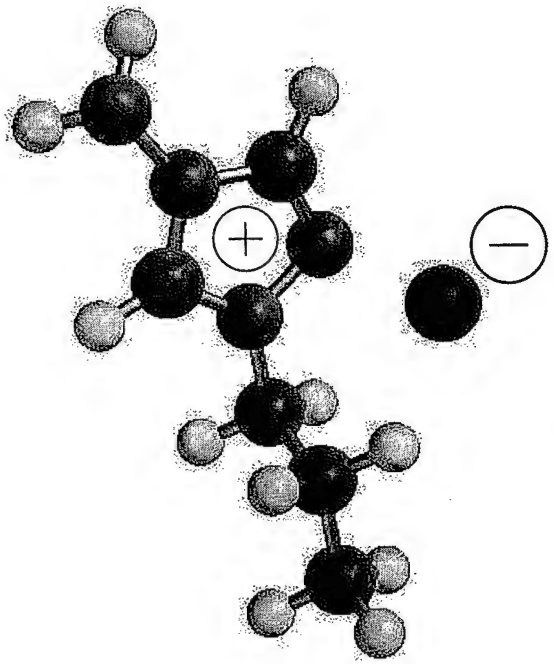
Packing in unit cell of 1-cyclopropylmethyl-4-amino-1,2,4-triazolium bromide

Energetic Ionic Liquids

Physical property trends of 1-n-alkyl substituted-4-amino-1,2,4-triazolium bromide salts roughly follow some trends but not all.
Substituted 4-amino-1,2,4-triazolium bromide salts have increasing melting points with increasing molecular weights, decomposition onsets that are relatively low, and densities which follow the expected decreasing trend with increasing alkyl chain length.

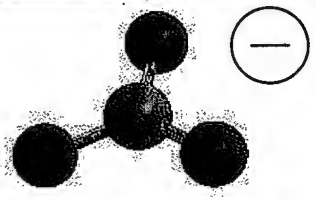
Substituted 4AT salts	m.p. (°C)	dec. onset (°C)	density (g/cm^3)
1-ethyl	63°	110	1.69
1-n-propyl	60°	120	1.56
1-isopropyl	90°	110	1.60
1-butyl	48°	130	1.46
1-n-pentyl	54°	130	1.37
1-n-hexyl	76°	120	1.34
1-n-heptyl	94°	120	1.30
1-n-octyl	80°	135	1.27
1-n-nonyl	81°	140	1.26
1-n-decyl	90°	135	

Energetic Ionic Liquids

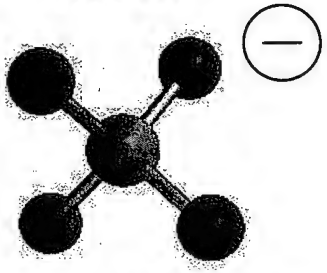


+ $AgNO_3$, $AgClO_4$, $AgN(NO_2)(CN)$

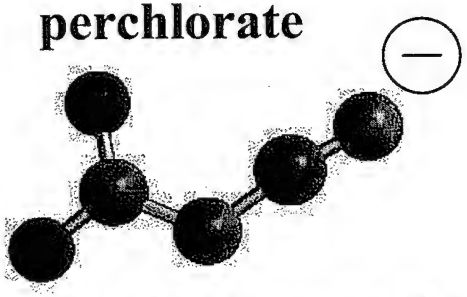
- AgBr



nitrate



perchlorate



nitrocyanamide

Synthesis is straight-forward and high yield with simple filtration to remove silver halide to give high purity ionic liquid. We have synthesized a large family of new salts based on this methodology.

Energetic Ionic Liquids

We have studied many but not all of the cation systems and have found some intriguing physical properties. The nitrate salts are much more thermally stable than their halide precursors and are extremely interesting.

1-substituted-4-amino-1,2,4-triazolium nitrate salts

Salt	melting point(°C)	decomp onset(°C)	density(g/cm^3, est.)
1-methyl	54	185	1.57
1-ethyl	5	185	1.39
1-n-propyl	37	190	1.35
1-n-butyl	-10	190	1.31
1-(2-ethanol)	10	180	1.48
1-methylcyclopropyl	56	190	
1-(2-propenyl)	10	165	

Energetic Ionic Liquids

The perchlorate salts are even more thermally stable than the nitrate salts and are interesting as well.

1-substituted-4-amino-1,2,4-triazolium perchlorate salts

Salt	melting point(°C)	decomp onset(°C)	density(g/cm^3, est.)
1-methyl	83	250	1.62(1.59m)
1-ethyl	5	195	1.54
1-n-propyl	0	190	1.49
1-n-butyl	39	240	1.44
1-(2-ethanol)	10	175	1.63
1-methylcyclopropyl	5	150	
1-(2-propenyl)	-11	185	

Energetic Ionic Liquids

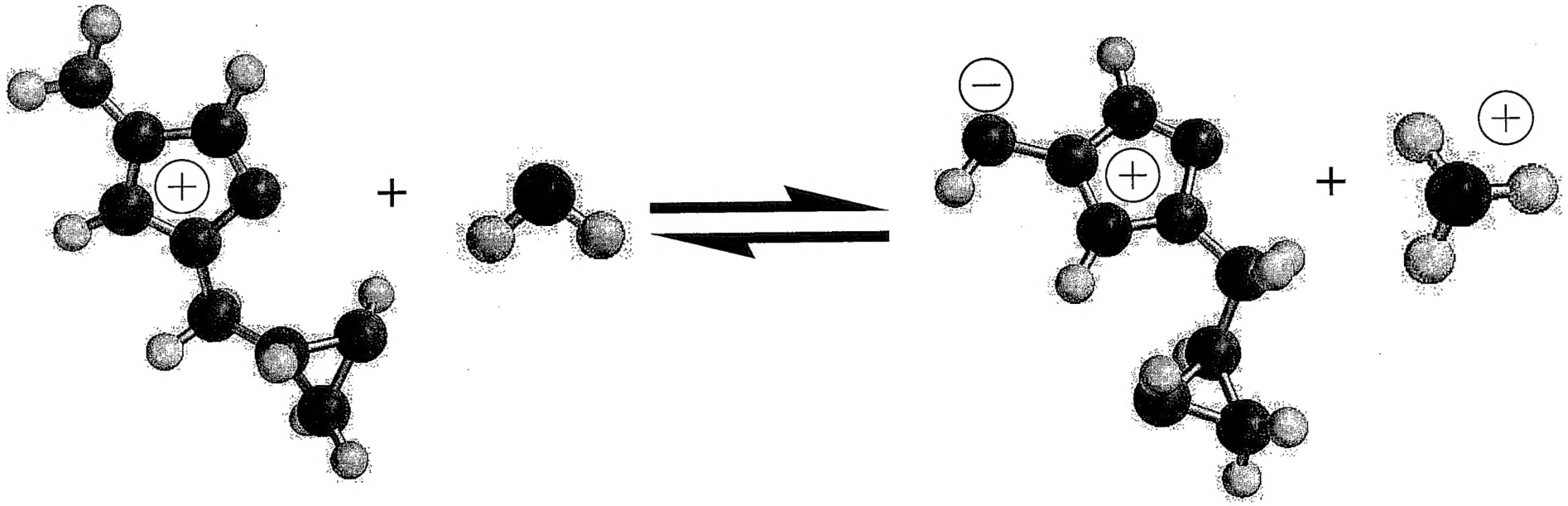
The nitrocyanamide salts are similar to the nitrate salts, are the least viscous, and have the lowest melting points.

1-substituted-4-amino-1,2,4-triazolium nitrocyanamide salts

Salt	melting point(°C)	decomp onset(°C)	density(g/cm^3, est.)
1-methyl	11	180	
1-ethyl	10	175	1.37
1-n-propyl	5	185	1.33
1-n-butyl	< 0 ?	175	1.30
1-(2-ethanol)	< 0 ?	175	1.43
1-methylcyclopropyl	-10	195	
1-(2-propenyl)	-11	185	

Energetic Ionic Liquids

The new energetic cations are weakly acidic in nature, aqueous solutions have a pH of around 5 which suggests the following equilibrium involving a zwitterionic 1-alkyl-4-amido-1,2,4-triazolium species. We have not tried to isolate this species yet to see if it exists. But similar chemistry has been observed with the acidic parent heterocycle 4-amino-1,2,4-triazole. This equilibrium could be one possible way for the ionic liquids to "come apart".



Energetic Ionic Liquids

Important issues for energetic ionic liquids

Structural features affect physical properties

- **Poor fit between cation and anion**
- **5 or 6 membered heterocyclic rings appear to be important with asymmetric substituents.**
- **Size, overall shape, and nature(basicity) of anion**
- **Hydrogen bonding can make major impact on physical properties**
- **intra- versus inter- molecular interactions especially melting point and viscosity**
- **Cation-anion interactions affecting melting point/viscosity**

Decomposition routes

- **pKa of parent heterocyclic ring**
- **basicity of counterion**
- **"active" hydrogens (-OH, NH_2, CHX)**